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COMPLETE SPECIFICATION

Stereoregular Polymerization of 1-Olefins in Monomer Solution

We, MOBIL OIL CORPORATION formerly known as SOCONY MOBIL OIL COMPANY, INC., a company organized under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York 17, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with the polymerization of olefins to solid, crystalline polymers. It is more particularly concerned with a novel, improved process for carrying out the stereospecific polymerization of butene-1 and higher 1-olefins and copolymerization thereof with propylene and ethylene.

Highly tactic polymers of 1-olefins have been prepared in the presence of catalyst systems comprising (A) a compound of a transitional metal of Group IVA, VA, VIA, and VIII of the Periodic Arrangement of the Elements, wherein the metal is present in a valance state lower than its maximum, and (B) at least one organometallic compound of metals of Groups II and III of the Periodic Arrangement of the Elements. In order to facilitate stirring and heat removal during the polymerization reaction and to improve contact with the catalyst, such polymerizations have been carried out in the presence of inert diluents, such as gasoline, paraffin oil, hexane, heptane, benzene and other hydrocarbons and mixtures thereof. In the case of polypropylene, it has been proposed to use liquid propylene as the diluent. In such polymerizations, the polymer, as it is formed, is dispersed in the diluent in the form of a slurry.

Polymerization processes utilizing the slurry technique, however, have certain disadvantages. The separation of polymer product, unreacted monomer, and inert diluent is an involved and relatively difficult procedure. Large amounts of diluent are used, which

must be separated by filtration or decantation methods. It is not always easy to recover the diluent in a sufficiently pure state to permit its reuse. More significantly, as the polymer product is in the solid state, the removal of catalyst residues is extremely difficult. Resort has been had to various involved extraction techniques, such as with aqueous acid solutions or with chelating agents. Also, in many cases polymer yield (parts per part of catalyst) and degree of tacticity have been relatively low.

It has now been found that butene-1 and higher 1-olefins can be homopolymerized or copolymerized with propylene or ethylene in high yields of polymer, usually having a high degree of tacticity, by a process which permits easy catalyst removal and product separation. It has been discovered that these advantages are achieved by using liquid butene-1 or higher monomer as a solvent in the polymerization process and by controlling conditions to maintain tactic polymer product in solution in the liquid monomer.

The term "tactic" is a generic term applied to solid polymers in which there is an ordered structure with respect to the configurations around at least one main-chain site of steric isomerism per conventional base unit. Numerous types of tacticity are recognised in the art. Within the contemplation of this invention, a measure of steric order is the weight per cent of the solid polymer that is insoluble in diethyl ether. A linear polymer that is insoluble in diethyl ether is considered to be tactic. Linear tactic polymers may be composed of isotactic or syndiotactic chains, blocks, or mixtures of these forms. The terms isotactic and syndiotactic are used in accordance with the definitions tentatively approved by commission on Macromolecules of the International Union of Pure and Applied Chemistry, as outlined in the Journal of Polymer Science, Volume 56, pages 153-161 (1962). Tactic polymers can contain sequences of atactic (that is, not tactic)

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units in conjunction with tactic sequences and still be insoluble in diethyl ether. They are tactic polymers within the contemplation of this invention.

5 In accordance with the present invention, there is provided a catalytic method for stereospecific bulk polymerization of a 1-olefin main monomer having 4-10 carbon atoms or copolymerization of a 1-olefin monomer having 4-10
10 carbon atoms as the main monomer with up to 20 mole per cent propylene or ethylene, to form a stereoregular polymer or copolymer, comprising operating in the liquid phase with sufficient main monomer to maintain a solution
15 of the stereoregular polymer or copolymer in the main monomer, and at a temperature between the lower cloud point and the upper cloud point of the solution.

In general, this invention provides a method
20 for producing tactic polymers of butene-1 and higher 1-olefins or tactic copolymers of butene-1 and higher 1-olefins with propylene or ethylene, which comprises contacting, in the liquid phase, a 1-olefin main monomer having 4 to
25 10 carbon atoms or a mixture of 1-olefin main monomer having 4 to 10 carbon atoms with up to 20 mole per cent propylene or ethylene, with a catalyst system comprising (A) a compound of a transi-
30 tional metal of Groups IVA, VA, VIA, and VIII of the Periodic Arrangement of the Elements wherein the metal is present in a valence state lower than its maximum and (B) at least one organometallic compound of metals
35 of Groups II and III of the Periodic Arrangement of the Elements, under conditions whereby liquid main monomer is a true solvent for the polymer or copolymer as it forms. Thus, the amount of liquid 1-olefin main
40 monomer used is in an excess, over the amount of 1-olefin that will react with the catalyst system to form tactic polymer, sufficient to form a solution of tactic polymer in 1-olefin main monomer having a concentration
45 tactic polymer. The polymerization temperature used will be between the lower Cloud Point and the upper Cloud Point of the solution of tactic polymer in its liquid monomer.

In other embodiments of this invention
50 small amounts of hydrogen can be employed, in order to control molecular weight of the polymer and to increase catalyst activity; and catalyst components can be removed from the solution of polymer in liquid monomer by
55 liquid-liquid extraction with de-oxygenated water.

The 1-olefin main monomer that is polymerized by the process of this invention is a 1-olefin having between 4 and 10 carbon
60 atoms, inclusive. It has the structure, $\text{CH}_2=\text{CHR}$, wherein R is an alkyl radical having between 2 and 8 carbon atoms. Non-limiting examples of the 1-olefin reactant include butene-1; pentene-1; 3-methylbutene-1;
65 hexane-1; 3-methylpentene-1; 4-methylpen-

tene-1; heptane-1; 4-methylhexene-1; octene-1; nonene-1; and decene-1. Preferably, the 1-olefin should be substantially pure (free of acetylene, oxygenated, or sulfur containing compounds.) Also, the 1-olefin should be dry
70 and oxygen free.

It is also within the contemplation of this invention to produce copolymers of a 1-olefin main monomer having between 4 and 10 carbon atoms with propylene or ethylene, in solution in the liquid main monomer. Thus, by way of non-limiting examples, there can be produced copolymers of butene-1 and ethylene, butene-1 and propylene, 3-methylbutene-1 and propylene, 3-methylpentene-1 and ethylene, and 3-methylpentene-1 and propylene, 4-methylhexene-1 and ethylene, and nonene-1 and propylene. In general, the amount of comonomer in the feed will be up to 20 mole per cent. When the amount of propylene or ethylene in the comonomer feed exceeds 20 mole per cent, the copolymer has a significantly reduced tacticity. Due to the greater polymerization rate of ethylene, however, it is preferred to use no more than 10 mole per cent ethylene comonomer.
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The catalyst system utilized in general, in making the polymers in accordance with this invention is composed of at least two components, one being a compound of a transitional metal of Groups IVA, VA, VIA and VIII of the Periodic Arrangement of the Elements in a reduced valence state, and the other being an organometallic compound of a metal of Groups II and III of the periodic Agreement of the Elements. The Periodic Arrangement of the Elements, as referred to herein, is that given in the Handbook of Chemistry, N. A. Large (Editor), Handbook Publishers, Inc, Ohio, 1946, pp. 58-59.
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Among the reducible transitional metal compounds suitable for the purpose of this invention are the heavy metal, inorganic compounds such as halide, oxyhalides, complex halides, hydroxides; and organic compounds such as alcoholates, acetates, benzoates, and acetyl acetonates, of the metals of Groups IVA, VA, VIA, and VIII of the Periodic Arrangement of the Elements. Such metals include titanium, zirconium, hafnium, thorium, uranium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and iron. The metal halides, particularly the chlorides are generally preferred. Titanium, zirconium and vanadium are the most active metals. The following heavy metal compounds are readily reducible: titanium tetrachloride, titanium tetrabromide, zirconium tetrachloride, vanadium tetrachloride, and zirconium acetylacetonate.
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These transitional metal compounds can be reduced to valance states lower than maximum valance by conventional procedures. As exemplified by titanium tetrachloride, it can be reduced to titanium trichloride and/or
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dichloride by hydrogen to a brown amorphous substance, which is converted into the violet crystalline form by heating at an elevated temperature in the order of 200°C. The reduction can be accomplished by heating titanium tetrachloride with metallic titanium or aluminum under pressure. This reduction can also be promoted by Friedel-Crafts halides. In the case of the aluminum reduction, the product will comprise reduced titanium chloride and aluminum trichloride. The reduction can also be effected by an organometallic compound of Group II or III to produce a crystalline titanium halide in a valence state lower than maximum. Suitable materials for this reduction are trialkyl aluminum and dialkyl aluminum halides. In practicing the present invention, the particular method of obtaining the transitional metal compound of reduced valence state is not pertinent. Indeed, many reduced compounds contemplated herein are commercially available.

The other component of the catalyst system is at least one organometallic compound of a metal of Groups II and III. These compounds will have at least one hydrocarbon radical, that is alkyl, cycloalkyl, aralkyl, alkaryl, or aryl, attached to the metal through a carbon atom. The other substituents in the organometallic compound include hydrocarbon radicals, halogen radicals, alkoxy, amino and hydrogen, or combinations thereof. Non-limiting examples of the organometallic compounds are triethylaluminum, tripropylaluminum, dipropylzinc, triisobutylaluminum, diethylmagnesium, diphenyl aluminum chloride, cyclohexyl - ethyl zinc, diethylaluminum bromide, diethyl - aluminum chloride, diethylaluminum iodide, ethylzinc chloride, propylmagnesium chloride, dipropylaluminum chloride, dioctylaluminum chloride, diisobutylaluminum hydride, phenylaluminum dihydride, cyclohexylbromo aluminum hydride, dipropylaluminum hydride, propyl zinc hydrate, ethylmagnesium hydride, and methoxyaluminum diethyl. Mixtures of two or more organometallic compounds can be used. A preferred mixture is diethylaluminum chloride and diethylaluminum iodide, usually in a ratio of 80 mole per cent chloride and 20 mole per cent iodide.

For the purpose of modifying catalyst and polymer characteristics, if desired, minor amounts of a third component can be used with the catalyst system of reduced transitional metal compound and organometallic compound. Such materials are well known and include carbides, acetylides, organophosphorus compounds, and Lewis bases.

In activating the reduced transitional metal compound (as $TiCl_3$) with an organometallic compound (as diethylaluminum chloride) various ratios can be used. Thus, the molar ratio of these two components (as Al/Ti) can

not greater than about 30 weight per cent range from 0.5 to 6 moles of organometallic compound per mole of reduced transitional metal compound. A ratio of 2:1 to 4:1 is preferred.

The catalyst system of reduced transitional metal compound and organometallic compound can be formed by conventional procedures. Particularly in batch operation, the catalyst can be formed by separately charging the catalyst components to the polymerization reaction zone, in the proper ratio, so that they are combined in the reaction zone or just prior to their entry therein. The reduced transitional metal compound is suitably charged as a slurry in liquid monomer. As the organometallic compound is usually liquid, a solvent need not be employed.

It is an important feature of the process of this invention that it is carried out using liquid 1-olefin main monomer as a true solvent. Under the operating conditions of the process, the tactic poly-1-olefin product dissolves in the monomer, or in the main monomer in the case of copolymers.

The yield of tactic polymer (that is, homopolymer or copolymer) is dependent, in part, upon the catalyst and varies with the catalyst system and the conditions. Such yield for a given catalyst and polymerization conditions is readily determinable by conventional means. It is usually expressed as parts tactic polymer produced per part reduced transitional metal compound.

In order to maintain the solution of polymer in main monomer, there must be present sufficient excess liquid main monomer over that which can enter into the polymerization reaction. Generally, the concentration of tactic polymer in the liquid main monomer should not exceed 30 weight per cent, because at higher concentrations efficient agitation and handling become extremely difficult. In preferred practice, the concentration of tactic polymer in liquid main monomer will be between 12 and 18 weight per cent. In order to maintain a selected concentration of polymer in 1-olefin main monomer, the ratio of monomer to catalyst can vary over a wide range dependent upon the catalyst activity and the reaction conditions employed. Accordingly, there can be charged to the polymerization reaction between 400 and 36,000 parts or more main 1-olefin per part of reduced transitional metal compound; all parts being by weight. Particularly in the case of a continuous process, the ratio can be determined in accordance with the formula:

$$\text{Ratio} = \frac{F_m}{F_c} = \frac{R \times a}{C_p}$$

wherein F_m is the monomer flow rate, F_c is the catalyst flow rate, R is the residence time, a is the catalyst activity, and C_p is the desired polymer concentration. Catalyst activity is

determined by the ratio of parts of weight of polymer over parts by weight of catalyst per hour.

5 A solution of a tactic homopolymer of
butene-1 and higher 1-olefins or of a tactic
copolymer of butene-1 or higher 1-olefin,
as the main monomer, with propylene or
ethylene as described above, in liquid C₃ - C₁₀,
1-olefin main monomer, exhibits a phenom-
10 non of having two cloud points. As the
solution is cooled, a temperature will be
reached at which solid polymer will come out
of solution. This temperature is called the
lower cloud point. On the other hand, as
15 the solution is heated a temperature will be
reached at which there will form a polymer-
rich phase and a polymer-lean phase. This
temperature is called the upper cloud point.
At temperatures between the two cloud points
20 there will exist a homogeneous solution of
polymer in main monomer. Accordingly, the
polymerization process of this invention must
be operated at temperatures between the lower
cloud point and the upper cloud point of the
25 solution of tactic polymer in its liquid olefin
monomer. The cloud points for a given
poly-1-olefin in its liquid monomer can be
readily determined by well-known methods.
In the case of polybutene-1, the polymerization
30 process will be operated at temperatures be-
tween 43 and 91°C. In preferred practice
the process is operated in 66°C.

The process of this invention is carried out
in the liquid phase. Accordingly, depending
35 upon the operating temperature, there must
be employed sufficient pressure to maintain the
main 1-olefin in the liquid phase. For each
1-olefin, the required pressure at the operating
temperature can be determined by means of
40 vapor pressure-temperature relationship curves,
such as by the Cox chart Method [Ind. Eng.
Chem. 15 592 (1923)].

It will be desirable in many cases to regu-
late the polymerization reaction, in order to
45 control the molecular weight of the polymer
product. To some extent this can be done
by adjusting process variables including tem-
perature, contact time and catalyst concentra-
tion, as is well known in the art. A more
50 feasible method is to add minor amounts of
hydrogen to the reaction to reduce molecular
weight. The amount of hydrogen used can
range from none up to 0.1 mole per cent,
based on 1-olefin charge.

55 In general, the residence time of 1-olefin
reactant and catalyst system in the polymeri-
zation reactor will be between 0.5 hour and 10
hours. Preferably it will be 3 hours.

60 Upon completion of the polymerization re-
action, the catalyst can be deactivated and
removed by conventional techniques and
manipulations, such as by treating with an
alcohol or an alcoholic solution of mineral
acid. Because, however, the polymer is in
65 solution in the process of this invention, the

catalyst can be most feasibly deactivated and
substantially completely removed by aqueous
washing of the solution of polymer in liquid
monomer. The polymer is maintained in
70 solution within the ranges of temperature and
pressure used in the reactor, as set forth above.
Suitably, substantially the same temperature
and pressure employed in the polymerization
reaction can be used, although higher temper-
75 atures, up to the upper cloud point, and cor-
respondingly higher pressure can be used.
In practice, the wash water is demineralized
and deoxygenated (to avoid oxidation of the
catalyst). If desired, acidic or basic com-
pounds, or chelating agents can be added
80 thereto. The reduced transitional metal
compound and reaction products of the organo-
metallic compounds will remain virtually com-
pletely with the aqueous phase. The amount
of aqueous wash employed can vary between
85 0.01 volume and 5 volumes per volume poly-
mer solution. Usually, 0.5-2.0 volume ratio
is preferred.

If it is desired, the washed polymer solution
can be treated by contact with absorbents,
such as alumina. Such treatment serves to
dry the polymer solution and to remove
residual traces of catalyst residues and of
acidic catalyst decomposition products. In
95 the usual practice of the process of this inven-
tion, however, such treatment is not necessary,
because satisfactory catalyst removal is ordin-
arily effected by aqueous washing alone.

After catalyst components have been re-
moved, the tactic polymer product is separated.
100 This can be done in several ways. In one
procedure, the pressure is reduced and the
1-olefin monomer is flashed off or distilled out,
leaving the tactic polymer. This procedure,
however, would involve handling relatively
105 large quantities of monomer. Another method
would involve maintaining liquid phase and
cooling the solution of polymer to precipitate
the polymer therefrom. It can then be
separated by filtration.

A particularly feasible method for separating
the polymer product is described in Serial No.
1051679, application 2527/65. As men-
tioned above, the solution of the polymer in
its liquid monomer exhibits two cloud points.
115 Thus, the solution is heated to a temperature
above the upper cloud point, with a corres-
ponding increase in pressure sufficient to main-
tain liquid phase. In order to obtain the
benefit of decreased viscosity and the resultant
ease in handling, it is desirable to use as high
a temperature as possible. This can be any
temperature above the upper cloud point and
up to the critical temperature of the 1-olefin
120 solvent. In the case the butene-1, therefore,
the solution of polybutene-1 in liquid butene-
1 is heated to a temperature between 91 and
145°C. A suitable temperature is 127°C.

When the solution of polymer in its mon-
omer is heated above the upper cloud point, as
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aforedescribed, there occurs a separation into two distinct liquid phases. The lighter phase is a polymer-lean phase which comprises liquid 1-olefin containing small amounts of polymer. The amount of polymer in the polymer-lean phase usually is less than one per cent. It is largely composed of atactic polymer and low molecular weight tactic polymer.

The heavier phase is a polymer-rich phase, that is, liquid monomer containing polymer in large amounts. In the case of butene-1, the concentration of polybutene-1 in liquid butene-1 in the polymer-rich phase will be in the order of 50 weight per cent. This phase can be readily separated and treated to recover the polymer product. Feasibly, this can be done by flashing off or distilling out the 1-olefin monomer. Another modification is to heat the separated polymer-rich phase to a temperature above the critical temperature of the monomer and to flash off the monomer, thus obtaining molten polymer product. This molten product can be fed directly to a hot melt extruder.

This method of separation has the advantage of reducing catalyst residue in the finished polymer to a low level. Upon heating the washed polymer solution to obtain two phases, if any trace amounts of catalyst residue remains in the washed solution, it will be approximately equally divided between the polymer-rich phase and the polymer-lean phase. Accordingly, residual catalyst residue remaining after washing will be reduced by 50 per cent in the final polymer.

The polymer-lean phase will contain small amounts of water and minor amounts of water-soluble decomposition products of the catalyst. This phase can be treated in various ways to recover pure 1-olefin monomer for recycling to the polymerization. For example, the polymer-lean phase can be cooled to a temperature approaching ambient temperature, being maintained under pressure sufficient to maintain liquid phase. This cooled phase can be water-washed to remove residual catalyst decomposition products and dried by contact with a suitable solid drying agent. Then, the 1-olefin monomer can be flashed or distilled off to recover reusable, pure 1-olefin.

In the examples and tables, the degree of tacticity of polymer product is measured as Isotactic Index (I.I.), that is, the weight per cent of polymer insoluble in diethyl ether. The Melt Index (M.I.) is determined in accordance with ASTM Designation: D-1238-62T, using condition "L". The Reduced Specific Viscosity (R.S.V.) is determined in accordance with ASTM Designation: 1601-61, and is the Specific Viscosity (Relative Solution Viscosity-1) divided by the concentration of polymer in decalin.

The process of this invention can be carried out batchwise. It is, however, particularly adapted to continuous processing. Referring

to the accompanying drawing, there is set forth a typical schematic arrangement for carrying out the process on a continuous basis. In the following example, there is described a continuous process specifically directed to the polymerization of butene-1. It will be recognised, however, that other 1-olefins, as mentioned above, can be polymerized in a similar manner.

EXAMPLE 1

In a typical continuous process schematically shown in the drawing, liquid butene-1 is introduced through a line 10. A portion of the liquid butene-1 was passed through line 11 and a desiccator or dryer 12, containing 3 Å pore size synthetic Zeolite A (described in B. P. 777,232). The desiccated liquid butene-1 was then passed through a line 13 into a catalyst preparation tank 14. Titanium trichloride in finely divided form was introduced through a line 15 into the catalyst preparation tank, wherein it was admixed with liquid butene-1 to form a slurry therein. The slurry of titanium trichloride in liquid butene-1 was removed from the tank 14 through a line 16 and pumped by a pump 17 through a line 18 into a polymerization reactor 19, at a feed rate of 1.33 g., titanium trichloride per hour.

The remainder of the liquid butene-1 introduced through line 10 was pumped by 20 through a line 21 into a butene desiccator or dryer 22. The dryer 22 contained Zeolite A, as aforedescribed. The dried liquid butene-1 was passed through lines 23 and 24 into the reactor 19. The total charge rate of liquid butene-1 was 30 pounds per hour. Diethylaluminum chloride (25% solution in heptane) was charged from a burette 25 and through line 26 into line 23. In line 23 the diethylaluminum chloride was commingled with the liquid butene-1 and charged to the reactor 19 through line 24 at a rate of 8.8 milliliters diethylaluminum chloride per hour. Hydrogen was charged through a line 27 and line 24 into the reactor 19 at a rate of 3.67 standard cubic feet per hour (SCFH). Recycle liquid butene-1 was charged into lines 27 and 24 through a line 28.

In the reactor 19, polymerization of butene-1 was effected at a temperature of 66°C. and under a pressure of 120 pounds per square inch gauge (p.s.i.g.). The average residence time in the reactor was 1.7 hours.

The effluent from the reactor, comprising polybutene-1 dissolved in liquid butene-1, catalyst and hydrogen, flowed from the reactor 19 through a line 29 into a catalyst extraction zone 30. The catalyst extraction zone was operated at a temperature of 73°C. Deoxygenated water was introduced through a line 31 into the catalyst extraction zone 30 at a rate of 13.2 pounds per hour. In the

extraction zone 30, the water was intimately mixed with the effluent from the reactor 19, in order to extract the catalyst therefrom.

5 The effluent from the extraction zone 30, comprising water containing catalyst decomposition products, polybutene-1 dissolved in butene-1, and hydrogen, was transferred from the extraction zone 30 through a line 32 into a water separation zone 33.

10 In the water separation zone 33, the solution of polybutene-1 in liquid butene-1 separated into an upper phase and the water containing catalyst decomposition products settled as the lower phase. Inerts and hydrogen were removed through a line 34. The lower, aqueous phase was continuously removed through a line 35. The solution of polybutene-1 was removed through a line 36 and pumped by a pump 37 through a line 38 into a preheater 39. In the preheater 39, the solution of polybutene-1 in liquid butene was heated to a temperature of 130°C. and the pressure was increased to 490 p.s.i.g. The heated solution was then transferred from the preheater through a line 40 into a polymer settling tank 41.

15 In the polymer settling tank 41, two phases separated. The upper, lighter phase comprised a polymer-lean solution, that is, 1 weight per cent low molecular weight and atactic polybutene-1 in liquid butene-1. This polymer-lean phase was removed through a line 42 and flashed in a surge tank 43.

35 Recycle butene was removed from the surge tank 43 through a line 44 and pumped by a pump 45 through a line 46 into a dessicator 47. In the dessicator 47, any water entrained in the recycle butene is removed by contact with a suitable dessicant, such as silica. The butene is then recycled through the line 28, as aforescribed.

40 The lower layer in the polymer settling tank 41 comprised a 50 weight per cent solution of tactic polybutene-1 in liquid butene-1. This solution was removed through a line 48. The solution withdrawn through line 48 was passed into a depressuring zone, not shown, wherein butene-1 was flashed off to obtain tactic polybutene-1 product.

50 In this continuous operation the catalyst productivity was 680 pounds of polymer per pound of titanium trichloride. The average I.I. was 90% and the M.I. varied between 0.25 and 0.33. Catalyst residues analyzed to 7 ppm titanium, 33 ppm aluminum, and 39 ppm chloride.

55 It will be evident from the foregoing example that the use of 1-olefin monomer as the solvent simplifies the overall process and facilitates handling of the product during the separation steps. There is an additional advantage in the use of liquid monomer solvent as compared to the same process wherein inert diluents are used. This is a marked

increase in polymer yield per unit of catalyst. The following examples illustrate this.

EXAMPLE 2 (Comparative)

A batch autoclave run was made to polymerize butene-1 in heptane diluent. There were charged to the autoclave 362 g. butene-1 and 1002 g. of heptane. The catalyst system was 1 g. titanium trichloride with diethylaluminum chloride, in an aluminum to titanium molar ratio of 2. The polymerization reaction was carried out for 1 hour at 77°C. There were obtained 27 g. of polybutene-1 having an I.I. of 64, a R.S.V. of 3.3, and a M.I. of 0.13.

EXAMPLE 3

80 A similar run was made to polymerize butene-1 using liquid butene-1 as the solvent. There was charged to the autoclave 1425 g. butene-1. The catalyst was 1 g. titanium trichloride with diethylaluminum chloride in an aluminum to titanium molar ratio of 2.5. The polymerization reaction was carried out for 60 min. at 74°C. There were obtained 53 g. polybutene-1 having an I.I. of 86, a R.S.V. of 5.1, and a M.I. of <0.1.

90 As has been mentioned hereinbefore, hydrogen can be used in the process of this invention to control molecular weight, as indicated by the reduced specific viscosity of the polymer. The use of hydrogen, however, has shown unexpected advantages of increasing yield and isotactic index. This is demonstrated in the following examples.

EXAMPLE 4

100 A batch autoclave run was made to polymerize butene-1 in liquid butene-1 at 54°C. The catalyst system was 1 g. titanium trichloride with diethylaluminum chloride in an aluminum to titanium molar ratio of 2.5. After 30 minutes of polymerization there were obtained 75 g. of polybutene-1. This polymer had an I.I. of 87 and a R.S.V. of 8.0.

EXAMPLE 5

110 Another run was carried out identical to that described in Example 4 with the exception that 38 millimoles of hydrogen were also charged to the autoclave. The yield of polymer was 142 g. and it had an I.I. of 93 and a R.S.V. of 4.5.

115 As was noted in the run described in Example 1, washing the reactor effluent with deoxygenated water effectively reduces the amount of catalyst residue in the polymer. Generally this treatment alone is sufficient, except for cases in which a product of very high purity is desired. Such a product can be achieved by additional absorption as illustrated in the following example.

EXAMPLE 6

120 In a run carried out as described in

Example 1 two catalyst removal techniques were used. In one case, the reactor effluent was water extracted. In a second case the polymer solution was water extracted and

then contacted with activated alumina absorbent. The comparative catalyst residue in the polymer product in each case was as follows:

	Catalyst Residues, ppm		
	Ti	Al	Cl
Water extraction only	1	Non-detectable	39
Water extraction plus adsorption (adsorbent: Activated alumina Fl)	1	—	Non-detectible

10 When using a dialkylaluminum halide as the co-catalyst in polymerization runs, it has been found advantageous to use mixtures of halides instead of the one alone. The advantages in using such mixtures are increased isotactic index, high activity, and lower molecular weight. As is demonstrated in the following examples, varying molar ratio of halides in such mixtures permits control of polymer properties without changing any variable in the process except the

co-catalyst composition.

EXAMPLE 7 — 11

A series of runs was carried out in the autoclave as described in Example 3. In each run there were used diethylaluminum iodide and diethylaluminum chloride in varying molar ratios. The molar ratio in each run and yield and pertinent properties of the polymer product are set forth in the following Table 1:

TABLE I

Example	Mole % Et_2AlI	Mole % Et_2AlCl	Activity	I.I.	R.S.V.	M.I.
7	0	100	532	84.8	2.52	0.68
8	10	90	366	85.1	1.69	1.90
9	20	80	362	91.9	1.79	1.66
10	33.33	66.66	335	93.2	1.61	2.83
11	100	0	116	94.3	1.87	2.41

30 The process of this invention can be used to prepare copolymers of butene-1 and higher 1-olefins with propylene or ethylene, charging up to 20 mole per cent propylene or ethylene. The following examples demonstrate such operation, using mixtures of butene-1 and propylene for illustrative purposes.

40 mixtures of butene-1 and propylene. In each run the amount of propylene charged was varied. Each run was carried out using a 1500 ml. charge of liquid butene-1/propylene with 0.5 g. TiCl_3 and 3.85 ml. diethylaluminum chloride, affording an Al/Ti mole ratio of 2.2. The runs were carried out at 66°C. for one hour, in the presence of 40 millimoles of H_2 . Pertinent data and results are set forth in Table II.

EXAMPLES 12 — 14

Three autoclave runs were made, using

TABLE II

Example	Charge Composition, Mole %		% Conv.	Activity	I.I.	R.S.V.	M.I.
	1-Butene	Propene					
12	94.4	5.6	16.0	282	86.0	3.2	0.68
13	87.0	13.0	17.2	308	81.0	2.8	0.65
14	69.7	30.3	16.3	314	29.6	2.4	1.50

From this data in Table II it will be apparent that copolymers can be made by the process of this invention. The amount of copolymer formed (% Conversion) is within the range of solubility in liquid butene-1, as set forth hereinbefore. By comparing Examples 13 and 14, it will be noted that, using more than 30 mole per cent propylene in the charge, results in a product of undesirably low crystallinity, as measured by I.I. Thus, Example 14 is a comparative example.

EXAMPLE 15

A run was carried out as described in

Example 1, using a charge of butene-1 and ethylene. This run was carried out at a temperature of 66°C. using a butene-1 flow rate of 30 pounds per hour and an ethylene flow rate of 1.25 to 5.1 standard cubic feet per hour. The catalyst was titanium trichloride promoted with 80 mole per cent diethylaluminum chloride and 20 mole per cent diethylaluminum iodide. The aluminum to titanium molar ratio was 3 and the residence time 4.4 hours. The copolymer produced exhibited the following methylene groups absorption:

Ethylene flow (SCFH)	Methylene group Absorption (IR)
1.25	0.008
3.4	0.020
5.1	0.027

WHAT WE CLAIM IS:

1. The catalytic method for stereospecific bulk polymerization of a 1-olefin main monomer having 4-10 carbon atoms or copolymerization of a 1-olefin monomer having 4-10 carbon atoms as the main monomer with up to 20 mole per cent propylene or ethylene, to form a stereoregular polymer or copolymer, comprising
 - operating in the liquid phase with sufficient main monomer to maintain a solution of the stereoregular polymer or copolymer in the main monomer,
 - and
 - at a temperature between the lower cloud point and the upper cloud point of the solution.
2. The method according to Claim 1 wherein the amount of 1-olefin monomer is in excess of that which will react with the catalyst system to form a tactic polymer or copolymer and is sufficient to form a solution of the tactic polymer or copolymer in the liquid 1-olefin monomer having a concentration not greater than 30 weight per cent tactic polymer or copolymer.
3. The method according to either of Claim 1 or Claim 2 wherein up to 0.1 mole per cent of hydrogen, based upon 1-olefin charge, is included in the charge.
4. The method according to any of Claims 1-3 wherein the polymerization is catalyzed with a catalyst system comprising component A which is a compound of a transitional metal of Groups IVA, VA, VIA and VIII of the Periodic

Arrangement of the Elements wherein the metal is in a valence state lower than its maximum,

and

at least one component B which is organometallic compound of metals of Groups II and III of the Periodic Arrangement of the Elements.

5. The method according to Claim 4 wherein component A is a titanium halide, desirably titanium trichloride, and

component B is at least one aluminum alkyl, desirably diethylaluminum chloride or a mixture of the chloride and diethylaluminum iodide.

6. The method according to Claim 5 wherein the Al/Ti molar ratio of the catalyst system is between 0.5 and 6.

7. The method according to any of Claims 1-6 wherein the polymerization is conducted at a temperature of 43-91°C. for a residence time of 0.5-10 hours.

8. The method according to any of Claims 1-7 wherein the 1-olefin main monomer is butene-1.

9. The method according to Claim 8 wherein the 1-olefin is butene-1 and the amount thereof is sufficient to form a solution of between 12 and 18 weight per cent tactic polybutene-1 in liquid butene-1 and is between 400 and 36,000 parts by weight of titanium halide, as determined by the formula

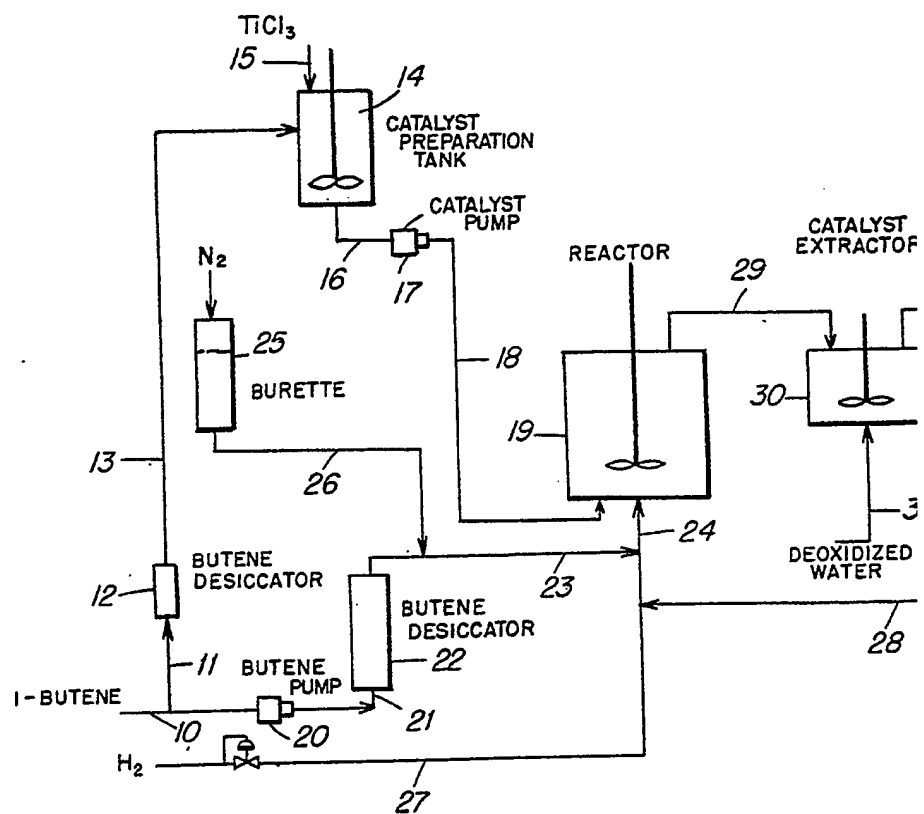
$$F_m = R \times a$$

$$\frac{F_c}{C_p}$$

wherein F_m is the amount of butene-1 used,

- 5 Fc is the amount of titanium halide used,
 R is the residence time,
 a is the catalyst activity
 and
 Cp is the concentration of poly-
 butene-1.
- 10 10. The method according to any of
 Claims 1—7 wherein the 1-olefin main mon-
 omer is butene-1 with propylene.
- 15 11. The method according to any of
 Claims 1—7 wherein the 1-olefin main
 monomer is butene-1 with ethylene.
- 20 12. The continuous method according to
 any of Claims 1—11 wherein the 1-olefin
 main monomer, with or without propylene
 or ethylene, and the catalyst system are con-
 tinuously introduced into a polymerization
 reaction zone, an effluent comprising a solu-
 tion of tactic polymer or copolymer in the
 liquid monomer and catalyst is continuously
 withdrawn from the zone, catalyst is removed
 from the solution of tactic polymer or co-
 polymer in the liquid monomer, and the
25 liquid monomer is continuously recycled to
 the zone.
- 30 13. The catalytic method for stereo-
 specific bulk polymerization of a 1-olefin main
 monomer having 4—10 carbon atoms or co-
 polymerization of a 1-olefin monomer having
 4—10 carbon atoms as the main monomer
 with up to 20 mole per cent propylene or
 ethylene, substantially as described by any
 of Examples 1, 3—13 and 15.
- 35 14. The catalytic method for stereo-
 specific bulk polymerization of a 1-olefin
 main monomer having 4—10 carbon atoms
 or copolymerization of a 1-olefin monomer
 having 4—10 carbon atoms as the main
 monomer with up to 20 mole per cent
 propylene or ethylene, substantially as here-
 inbefore described and shown in the accom-
 panying drawing.
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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale

